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The Effect of Acid Neutralization on Analytical Results Produced from SW846 Method 8330 after the Alkaline Hydrolysis of Explosives in Soil

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Abstract

Alkaline hydrolysis has been used in several laboratory studies and field demonstrations for the treatment of energetic compounds (particularly, 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)) in soil. The application of alkaline hydrolysis for treatment of soil involves mixing a caustic source material with soil. Two caustic materials have been explored, calcitic hydrated lime [$\text{Ca}(\text{OH})_2$, HL] and sodium hydroxide (NaOH). Evaluation of explosives removal is routinely performed using SW-846 Method 8330. This method was developed before the advent of alkaline hydrolysis treatment, and recent studies have indicated that some errors can occur when this method is applied to alkaline hydrolysis samples. This report documents the results of a field study conducted to demonstrate the issue of false degradation in field-collected samples. The field study was followed by two laboratory studies: the first to confirm false degradation as a phenomenon and the second to develop an appropriate acid neutralization method. Results proved that false degradation can occur with alkaline hydrolysis (AH) samples, particularly if residual caustic material and moisture are present in the sample. Treatment systems using HL are more prone to extraction errors than systems using NaOH, although neutralization improves the accuracy of both treatment approaches. ERDC-EL has developed a neutralization method that can be used for alkaline hydrolysis approaches using up to 10% caustic addition (most systems are less than 5%) and a combination of H_3PO_4 and NaH_2PO_4 . For remedial actions using alkaline hydrolysis, the scope of work for the action should include neutralization of all post-treatment samples, with appropriate control samples prepared in order to ensure that neutralization is achieved.

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Preface

The work reported herein was conducted at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS. Funding for the work described herein was provided by the Innovative Technology Advocate of the Formerly Used Defense Sites Program, which is managed by Sam Bass, United States Army Corps of Engineers.

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This study was conducted under the direct supervision of W. Andy Martin, Branch Chief, Environmental Engineering Branch (EP-E); and Warren P. Lorentz, Division Chief, Environmental Processes and Engineering Division (EPED); and under the general supervision of Dr. Elizabeth Ferguson, Technical Director (EL).

At the time of publication of this report, Dr. Beth Fleming was the EL Director, COL Kevin J. Wilson was Commander of ERDC, and Dr. Jeffery P. Holland was Director of ERDC.

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Unit Conversion Factors

Multiply	By	To Obtain
Acres	4,046.873	square meters
acre-feet	1,233.5	cubic meters
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
Feet	0.3048	meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
Hectares	1.0 E+04	square meters
Inches	0.0254	meters
Microns	1.0 E-06	meters
miles (U.S. statute)	1,609.347	meters
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter
pounds (mass) per cubic inch	2.757990 E+04	kilograms per cubic meter
pounds (mass) per square foot	4.882428	kilograms per square meter
pounds (mass) per square yard	0.542492	kilograms per square meter
square feet	0.09290304	square meters
square inches	6.4516 E-04	square meters
square miles	2.589998 E+06	square meters
square yards	0.8361274	square meters
tons (long) per cubic yard	1,328.939	kilograms per cubic meter
tons (2,000 pounds, mass)	907.1847	kilograms
tons (2,000 pounds, mass) per square foot	9,764.856	kilograms per square meter
Yards	0.9144	meters

Acronyms

ACN	Acetonitrile
AES	Atomic Emission Spectrometry
AH	Alkaline hydrolysis
ANOVA	Analysis of Variance
CE	Camp Edwards
DI	Deionized water
DOD	Department of Defense
EL	Environmental Laboratory
EPA	Environmental Protection Agency
ERDC	Engineer Research and Development Center
FUDS	Formerly Used Defense Sites
ft	foot
ft ³	cubic foot
g	gram
HL	Hydrated lime [see Ca(OH) ₂]
HPLC	High-performance liquid chromatography
hrs	hours
IAAP	Iowa Army Ammunition Plant
ICP	Inductively Coupled Plasma
L	Liter
lb	pound
LOOW	Lake Ontario Ordnance Works
LSAAP	Lone Star Army Ammunition Plant
MDL	Minimum Detection Limit
mg	milligram
min	minutes
m ³	cubic meter
nd	non-detect
PB1	Soil from the Plum Brook Ordnance Works, West Reservoir 2B Area

PB2	Soil from the Plum Brook Ordnance Works, Pentolite Road Area
PBOW	Plum Brook Ordnance Works
ppb	Parts per billion
ppm	Parts per million
r	Correlation Coefficient
rpm	revolutions per minute
r ²	Coefficient of Determination
s	second
S	Standard Deviation
μg	microgram
μg	micrometer

Energetic Compounds

ADNT	2,4/2,6-amino-dinitrotoluene
DNB	1,3-dinitrobenzene
DNT	2,4-dinitrotoluene
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNT	2,4,6-trinitrotoluene

Other Compounds

CaCl	Calcium Chloride
CaCO ₃	Calcium carbonate
Ca(OH) ₂	Calcitic hydrated lime
HCOO ⁻	Formate
HCl	Hydrochloric acid
H ₃ PO	Phosphoric acid
H ₂ SO ₄	Sulfuric acic
NaOH	Sodium hydroxide
NaH ₂ PO ₄	Mono-basic form of phosphoric acid or sodium phosphate
NO ₂ ⁻	Nitrite
OH ⁻	Hydroxide ion

1 Introduction

Alkaline hydrolysis has been used in several laboratory studies (Österreicher-Cunha et al. 2003; Davis et al. 2006, 2007; Felt et al. 2002; Larson et al. 2008a, Medina et al. 2007) and field demonstrations (Johnson et al. 2010; Larson et al. 2008b; Waisner et al. 2008, Britto et al. 2010, Tetra Tech 2008a) and full-scale remediation (Tetra Tech 2008b, Shaw Environmental 2008) for the treatment of energetic compounds (particularly, 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)) in soil. Each of these tests demonstrated effective transformation rates in the treated soils, with removals of 90 to 99%. Observed first-order rates were relatively fast in aqueous phase kinetic tests conducted at pH >10: 0.23 hr⁻¹ for TNT and 0.18 hr⁻¹ for RDX. Rates in soils are also reasonable for treatment (TNT half-life of 0.15 days for soil from Camp Guersney and RDX half-life of 0.28 days for soils from both Fort Wainright and Crane Naval Weapons Station). These rates are comparable to those achieved by other treatment approaches, such as bioremediation. Alkaline hydrolysis reactions break down energetic compounds using different chemical pathways from those of the reductive techniques like bioremediation. For example, reaction products, like amino-DNT, produced by TNT bioremediation are often regulated and can accumulate in the soil. Hydrolysis does not form these compounds and appears to lead to ring cleavage, yielding final transformation products like formate, which are easily degraded by soil microorganisms.

The application of alkaline hydrolysis for treatment of soil involves mixing of caustic source material with soil. Two caustic materials have been explored, calcitic hydrated lime (Ca(OH)₂, HL) and sodium hydroxide (NaOH). These materials can be applied to soil as pellets or powders, or, in the case of NaOH, dissolved and applied as an aqueous amendment. Treatment can be conducted using a landfarming approach (where caustic materials are plowed, disked, or mixed using a bulldozer blade), in a modified composting scenario (windrows with caustic material addition, turned periodically for mixing), in slurries, or topically applied, with or without mixing, depending on contaminant depth. In fact, flexibility in treatment approaches is an attractive feature of the alkaline hydrolysis technology.

Destruction of explosives via alkaline hydrolysis actually occurs in soil pore water. When the caustic material is applied to the soil, it will dissolve into any soil pore moisture, elevating the pH of that water (Figure 1). In order for degradation to occur, the soil-adsorbed contaminant must dissolve and/or desorb from the soil phase and enter the caustic soil pore water (Figure 2). When it does, the contaminant encounters the elevated pH, and becomes susceptible to nucleophilic attack, resulting in reduced explosives concentrations in soil. Figure 2 shows the dissolution process of particulate TNT. Smaller particles are dissolved rapidly; larger particles more slowly. Soil pH is typically reduced over time via several mechanisms, besides reaction with the energetic compounds: reaction with carbonic acid (from the dissolution of carbon dioxide in the atmosphere), buffering by soil minerals, reactions with humic or organic acids, and gradual leaching of the caustic material (Brooks et al. 2003, Larson et al. 2007).

As mentioned above, both HL and NaOH have been successfully used as treatment materials, and both materials essentially work the same way – they both dissolve in the soil pore water elevating its pH to facilitate hydrolysis reactions. However, HL and NaOH have some key differences. The amount of

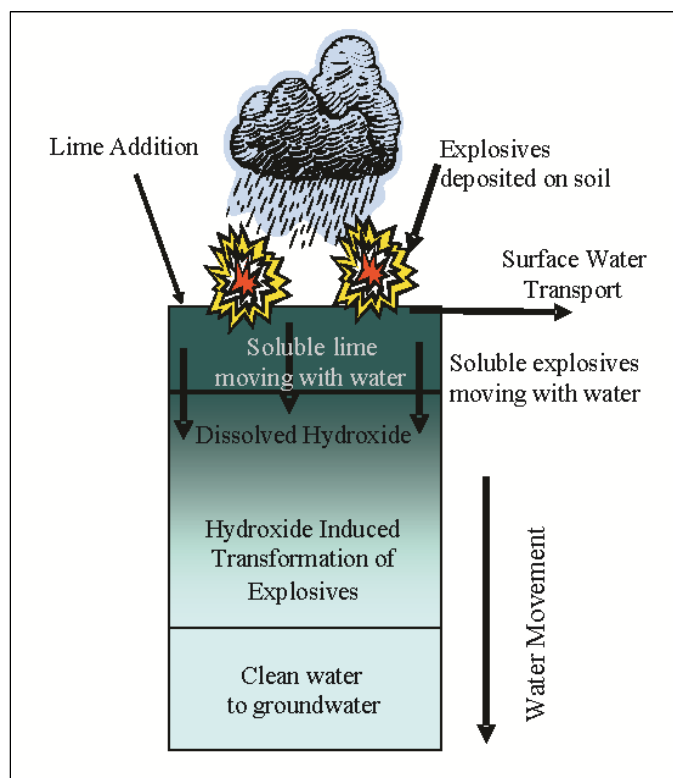


Figure 1. Schematic illustrating the process of alkaline hydrolysis of energetic compounds in soil

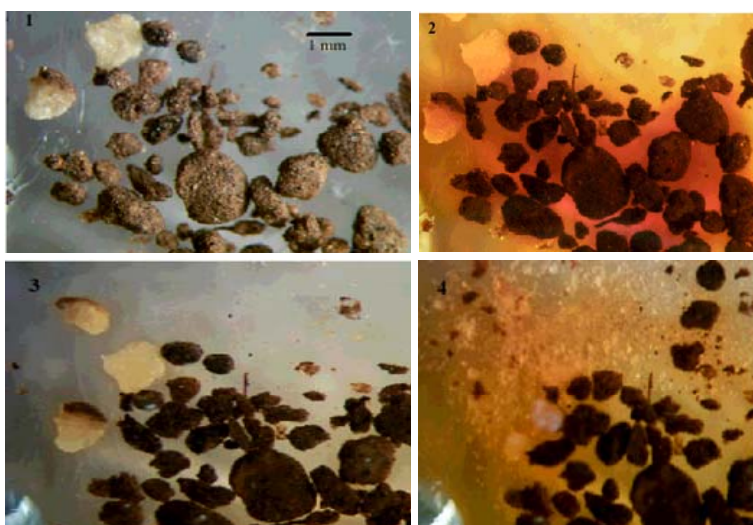


Figure 2. Microscale characterization of the process of dissolution of particulate TNT in simulated alkaline pore water (Larson et al. 2008a)

HL added typically raises pH of soil pore water to pH 10.5 - 11. Because HL has a limited solubility in water (approximately 1,000 mg/L), the amount of lime used to overcome the buffering capacity of the soil and achieve these pH levels is far in excess of that which can be solubilized by the maximum amount of moisture that can be retained in the soil. This means that treatment can typically result in a long equilibrium phase. This long equilibrium phase is often beneficial as it maintains the elevated soil pore water pH over the period required for explosives to dissolve, desorb and react. NaOH tends to dissociate completely in water, and because of that, NaOH can increase the soil pH to over 12, and as high as 14. Because NaOH is far more soluble (>1000 g/L), if the same mass was applied to a given soil, it will generally dissolve more completely than HL, resulting in a shorter equilibrium phase.

These differences could result in treatment issues. Since NaOH can achieve a higher pH, it may be able to treat a wider range of contaminants or result in faster reactions. However, the higher pH could become problematic, as soils with pHs higher than 12 can be classified as RCRA hazardous wastes. The lower solubility of HL results in a lower pH, but also results in greater persistence of the caustic material. This means that for an identical amount of caustic material added, it is likely that the HL will provide treatment over a longer time frame than the same amount of NaOH. Since the solubility of explosive contaminants can limit the transfer of these compounds into the liquid phase over a given time, this can be an important advantage for HL treatment.

In spite of the high solubility of NaOH, it is still possible for some of the NaOH applied during soil remediation to remain undissolved. Although this is generally unlikely, it can occur due to inadequate soil moisture content, and /or inadequate mixing. NaOH is usually applied in the form of anhydrous pellets and mixed into the soil (Figure 3). If the soil is relatively dry to start with, the water-withdrawing properties of anhydrous amendments can exacerbate the situation by further reducing the moisture content of the soil.



Figure 3. Application of anhydrous pellets of NaOH for alkaline hydrolysis of soil using a windrow treatment configuration at the former Plum Brook Ordnance Works (PBOW)

Evaluation of any treatment method requires reliable analytical methods. Evaluation of explosives removal is routinely performed using SW-846 Method 8330 (1999). This method was developed before the advent of alkaline hydrolysis treatment, and recent studies have indicated that some errors can occur when this method is applied to alkaline hydrolysis samples. During Method 8330 sample extraction, acetonitrile (ACN) is added to an air-dried soil and the mixture is sonicated for 18 hours. This process results in a portion of the explosives partitioning into the ACN phase. However, since the analytical method calls for air-drying the soil samples prior to extraction, complete drying of the sample is not achieved and residual water can be present in the sample being extracted. This water, which is highly miscible with ACN, exposes the sample being extracted to residual caustic material in solution during the 18 hour sonication, resulting in rapid destruction of the explosive through a similar alkaline hydrolysis process occurring on-site. This can lead to analytical values of explosives concentrations in the soil matrix that are far lower than the actual value of the sampled soil – giving the impression of false degradation. This can adversely affect data quality for post-treatment (i.e., confirmatory) sampling during soil remediation projects. Reviewing data from several studies has shown evidence of this effect, either extremely high contaminant

transformation rates in the treated soils or very high variability of these rates (Österreicher-Cunha et al. 2003; Davis et al. 2006; Waisner et al. 2008).

In order to resolve the analytical challenges associated with monitoring the actual concentrations of explosives in soil samples during alkaline hydrolysis treatment, a series of comparative studies were performed. Field and laboratory studies were conducted to demonstrate the false degradation phenomena. Then, additional laboratory studies were conducted to develop methods to address this effect. These studies investigated explosives dissolution and desorption from soil into pore water and techniques to neutralize both HL and NaOH in soil samples prior to sonication. Universal acid neutralization processes were developed to eliminate the extraction effect, and these can easily be applied to Method 8330.

2 Materials and Methods

Overview

The project consisted of three parts. A field study was conducted to demonstrate the issue of false degradation in field-collected samples for a site contaminated with TNT. A second study — a laboratory study — was conducted to confirm the issue of potential false degradation in lime-treated samples for a single soil contaminated with TNT. Finally, a laboratory study was conducted to develop an appropriate acid neutralization method — demonstrated with several soil types, two forms of caustic addition (HL and NaOH), and for both TNT and RDX.

Field Study. Demonstration of False Degradation and the Effect of Acid Neutralization from a Full-Scale Alkaline Hydrolysis Remediation Project

Soil

Soil was obtained from an ongoing remediation effort that was conducted in 2011 at the former Plum Brook Ordnance Works (PBOW) located in Sandusky, Ohio. The soils were known to contain both TNT and DNT. The soils were undergoing active alkaline hydrolysis remediation by Tetra Tech, Inc. under the guidance of the Huntington District of the U.S. Army Corps of Engineers. The remediation approach involved excavating the soils and placing them in 9 windrows labeled W1 through W9. In the field, NaOH was mixed into the soil in a granular form along with a ferric chloride solution. The NaOH was added at a rate of 2% on a weight to weight basis. Samples from these 9 windrows were collected at three time periods: T1 was collected at the start of the operation, T2 was about the midpoint of the 6-week treatment, and D was at the end of the 6-week treatment. The intermediate samples (T2) were only collected for the first 3 windrows (W1-W3). Figure 4 shows the initial appearance of dry soil with sodium hydroxide pellets visible after mixing.

Neutralization of Soil pH

Neutralization of soil pH prior to extraction was accomplished by placing approximately 20 grams of soil in a plastic pan and adding 20-mL of acid (two different acids were used, and are described below). The resulting soil



Figure 4. Sodium hydroxide pellets visible in soil after initial soil mixing.

slurry was periodically mixed with a metal spatula until ebullition of gas from the slurry was insignificant. 6.15-N HCl was used for neutralization. However, after pH values significantly below 4 were measured in some samples, the acid used was switched, and 20-mL of 5-M sodium phosphate (NaH_2PO_4) was added to soil samples. After neutralization was completed, the soil sample was mixed in the pan and appropriate amounts were collected for SW-846 Method 8330 extraction and pH and moisture content analysis.

Laboratory Study 1. Confirmation of False Degradation and the Acid Neutralization Effect

A total of nine test conditions were established to explore the false degradation effect in a laboratory setting. The test conditions included four levels of lime addition, four levels of soil moisture, and two conditions with pre-extraction acidification. Two of these conditions were controls without lime addition: condition A followed a normal extraction procedure, and condition I was acidified prior to the extraction procedure to determine whether acidification produced any significant impact on extraction or analysis.

Tests were conducted in triplicate with a well-homogenized air-dry soil (soil moisture = 1.52%, Standard Deviation (S) = 0.004%, $n = 3$) from a site contaminated with high levels of TNT (Plum Brook Reservoir 2B Burn

Area). Tests were conducted in 50-mL polypropylene centrifuge tubes. 15-g samples of the soil were placed in each test tube. Lime was added to tubes according to the conditions described in Table 1 and mixed in with a spatula. Tubes with lime were then placed on a laboratory rotator, turning at approximately 20 rpm for 30 minutes to allow the lime to mix into the soil. Deionized water (DI) was then added to each tube according to the conditions described in Table 1 and mixed into the soil with a spatula. For all conditions except C and I, approximately 10-g moist soil was removed from the test tube and placed in a 40-mL amber-glass vial with 20-mL of ACN, and the vials were placed in a sonicating water bath for 18 hours. ACN was added to each vial within 10 minutes of DI addition. The remaining soil was used for moisture content analysis.

Table 1. Experimental Conditions.

Condition	Moisture	DI	Lime	Lime	Acidified
A	21.5%	3.00 mL	0%	0.00 g	
B	21.5%	3.00 mL	2%	0.30 g	
C	21.5%	3.00 mL	2%	0.30 g	X
D	11.5%	1.50 mL	2%	0.30 g	
E	6.5%	0.75 mL	2%	0.30 g	
F	1.5%	0.00 mL	2%	0.30 g	
G	21.5%	3.00 mL	4%	0.60 g	
H	21.5%	3.00 mL	1%	0.15 g	
I	21.5%	3.00 mL	0%	0.00 g	X

For conditions C and I, 10-mL of 2.5-N sulfuric acid (H_2SO_4) was added following mixing of lime into the soil. The test tubes were hand agitated for approximately 30 seconds and placed on a rotator for approximately 2 hours. Test tubes were vented at approximately 15-minute intervals to relieve gas pressure due to the reactions. The test tubes were then centrifuged at a relative centrifugal force of 2500-g for 15 minutes. The supernatant was withdrawn for explosives analysis and the volume was recorded. At this point, the soil in these conditions was handled in a manner identical to all other conditions.

Following sonication, 5 mL of extract was withdrawn from each vial and placed in 20-mL glass vials with 5 mL 0.5% CaCl solution. The vials were vortexed and allowed to settle for 15 minutes. Four mL of the mixture was

filtered through 0.45- μ m glass-fiber filters into amber sample vials and refrigerated until analyzed.

TNT analyses were conducted by high performance liquid chromatography (HPLC) with a C-18 column and 50:50 water:methanol carrier solution.

Laboratory Study 2. Explosives Dissolution and Development and Testing of Acid Neutralization

Soil Preparation

A series of soils with a wide range of soil properties, explosives concentrations, and contaminant/soil weathering were selected so those conducting this study would gain a better understanding of the rate of explosives dissolution/desorption in water. The varied nature of the soils also enabled study participants to more easily develop an effective neutralization technique. The 6 soils came from 5 separate locations and were historically contaminated with explosives as a result of both ordnance use and production activities. Table 2 lists the soils used and the abbreviations that will be used to identify these soils throughout the remainder of the report.

Table 2. Soils used in the dissolution/desorption and neutralization experiments.

Name	Sample ID	Soil type	pH
Plum Brook 1 (West Reservoir 2B area)	PB1	Medium sand with clay	7.9
Plum Brook 2 (Pentolite Road Area)	PB2	Medium sand with silt and clay	8.4
Lake Ontario Ordnance Works	LOOW	Coarse sand/loam	7.7
Camp Edwards	CE	Sandy silt	4.9
Iowa Army Ammunition Plant	IAAP	Silty clay	8.1
Lone Star Army Ammunition Plant	LSAAP	Medium sand	8.0

Each soil sample (Table 2) was spread onto stainless steel trays to a thickness of one half centimeter and allowed to dry in an environmental chamber at 55 °C over a period of 5 days and nights, as specified by EPA method 8330. After that period, the samples were evaluated for obvious moisture and determined to be dry under the operational definition associated with SW-846 Method 8330.

The samples were ground using a mortar and pestle in batches weighing less than 50 grams in order to reduce particle size and provide a representative sample from which sub-sampling could be reliably achieved.

This operation was performed behind a laboratory shield under a ventilated fume hood.

Once ground, the samples were passed through a #200 soil sieve which passes particles smaller than 0.075 mm. Oversize materials, such as rocks or vegetative materials, were removed from the sample.

Dissolution of Explosives in Water

In order to evaluate the rate of migration of explosives from the solid phase to the dissolved phase, a series of kinetic experiments were performed in 20-ml amber vials. These involved 4 soils (IAAP, CE, LOOW and PB1), investigating the dissolution of TNT and RDX. Two (2) grams of soil and 10 mls of water were allowed to mix and 5 mls of water was periodically removed, filtered, and analyzed in order to determine the amount of explosives that transitioned from the solid to the liquid phase. After each 5 ml removal, an additional 5 mls of deionized water was added to the sample to return the total volume to 10 mls.

Acid Neutralization / Buffering

The dosing level for the alkaline hydrolysis material was 10% by soil dry weight. These soils were allowed to air dry and water content was between 3 and 5%. The NaOH dosing rate was calculated by determining the same number of OH⁻ equivalents as 10% HL. There are 2 moles of HL for each mole of NaOH.

Two separate neutralization studies were performed. The first study used a stoichiometric equivalent of the mono-basic form of phosphoric acid (NaH₂PO₄) in order to attempt to neutralize both HL and NaOH caustic reagents prior to sample drying, addition of ACN, sonication, sample preparation, and analysis. At set periods of time following addition of the caustic agent, an aqueous solution containing one equivalent of the NaH₂PO₄ was added to the sample, and mixed thoroughly. The sample was then allowed to air-dry for 7 days. The dried sample was extracted using ACN and sonicated for 18 hours prior to analysis.

The second neutralization study used a combination of mono-basic and di-basic phosphoric acid (one equivalent each in neutralization 1, or two equivalents phosphoric acid and one equivalent of NaH₂PO₄ in neutralization 2). This study was tailored for the neutralization of samples treated with hydrated lime.

Soil Extraction and Analysis

Soil samples were extracted following the procedures outlined in US EPA SW-846 Method 8330 (1999). Two g of air-dried (55C) soil and 10 ml of ACN were placed in a test tube and the mixture was combined in a Vortex mixer for 1-min and sonicated in the dark at 5 °C for 18 hr.

The explosives concentrations of the different soils were quantified using a DIONEX HPLC system equipped with a C-18 reverse phase column and a photodiode array detector which measured absorbance at 254 nm. A CN column was used for confirmatory analysis. The mobile phase was 50:50 (v:v) methanol:organic-free reagent water. The flow rate was set at 1.0 ml/min and a 25 µl injection volume was used. The MDL for explosives under these analysis conditions is 0.02 mg/L.

Matrix spikes are an accepted method of quantifying the recovery of the compound of interest guard against false negatives. In a matrix spike, the matrix (soil, groundwater, surface water, etc.) has a spike of the contaminant of interest added to it and is thoroughly mixed. This sample is then extracted and analyzed. The recovery of the spike can be quantified. Matrix spikes are included as part of the EPA Method 8330. Their value is critical in explosives studies, particularly in those involving alkaline hydrolysis.

3 Results and Discussion

Field Study Results

The measured pH of soils, both before and after neutralization, is presented in Figure 5. Before neutralization, the pH of all soils tested was between 12.0 and 13.3. Following neutralization, the pH of most soils was between 4 and 7. The pH of samples W3-T2, W5-T1, W6-T1, and W7-T1 were all below 2, which was lower than the desired range of 4 to 8. The occurrence of an excessively low pH in neutralized samples was avoided in future samples by switching the acid used from HCl to NaH_2PO_4 . The pH of samples W3-T1 and W4-T1 were not measured.

The results of TNT and DNT analysis of soils by Method 8330 by both the standard extraction method and with pH neutralization prior to extraction are presented in Figure 6 and Figure 7, respectively. In general, where these compounds were detected, neutralization of the soil pH prior to extraction resulted in higher concentrations of these compounds being detected. Two exceptions, samples W6-T2 and W7-T2, did occur with TNT. In all cases, the measured values for both TNT and DNT were below the method detection limits by the final samples (-W#-D).

In all cases, the measured values for both TNT and DNT by the standard extraction method were below the method detection limits by the final samples (-W#-D). However, DNT was still detectable in the final samples from windrows W5, W6, and W7 when the pH of the soil was neutralized prior to extraction. Results obtained by using pH-neutralization of the soil samples prior to extraction also show the progress of explosives destruction during the remediation project.

Laboratory Study 1. Confirmation of False Degradation and the Acid Neutralization Effect

The field study confirmed that acid neutralization greatly affects the results of an actual field application of alkaline hydrolysis. However, variability in the field samples creates variability in the results that required confirmation by a focused laboratory study. Figure 8 shows the results of a study in which identical soils from the Plum Brook Ordnance Works (Reservior 2B burn area) were sampled right after being treated with different amounts of HL

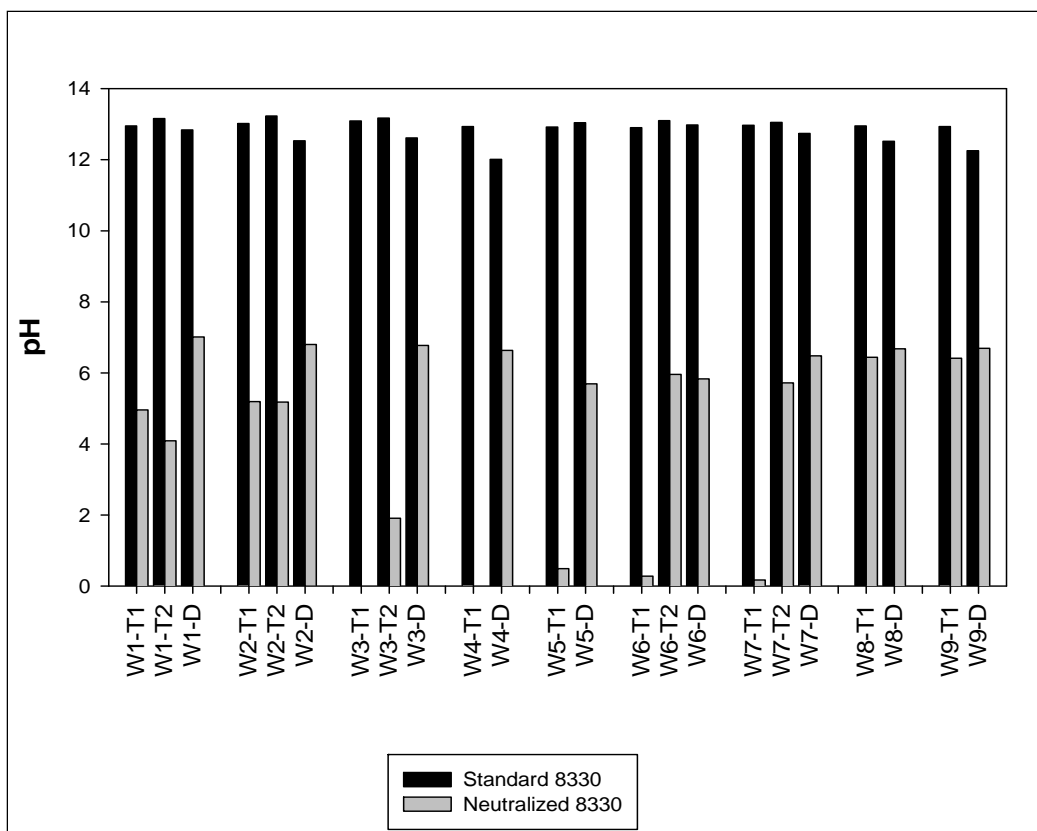


Figure 5. pH of samples collected from PBOW alkaline hydrolysis remediation project and effect of neutralization.

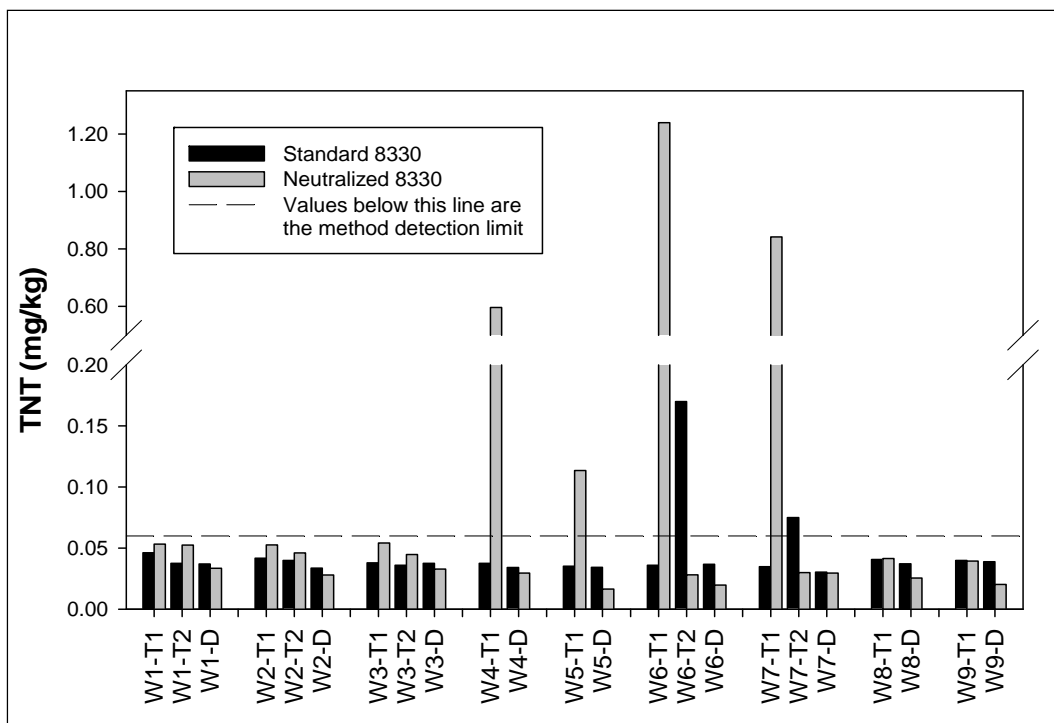


Figure 6. TNT concentrations of soils collected from the PBOW remediation project, comparing neutralized and non-neutralized samples.

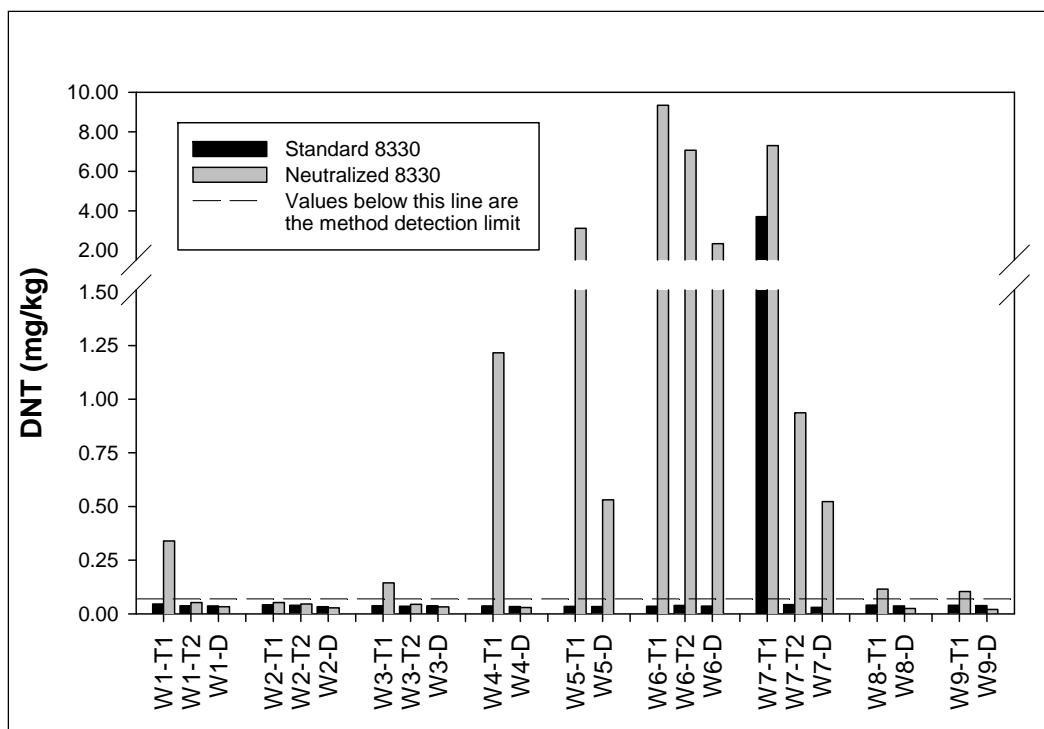


Figure 7. DNT concentrations of soils collected from the PBOW remediation project, comparing neutralized and non-neutralized samples.

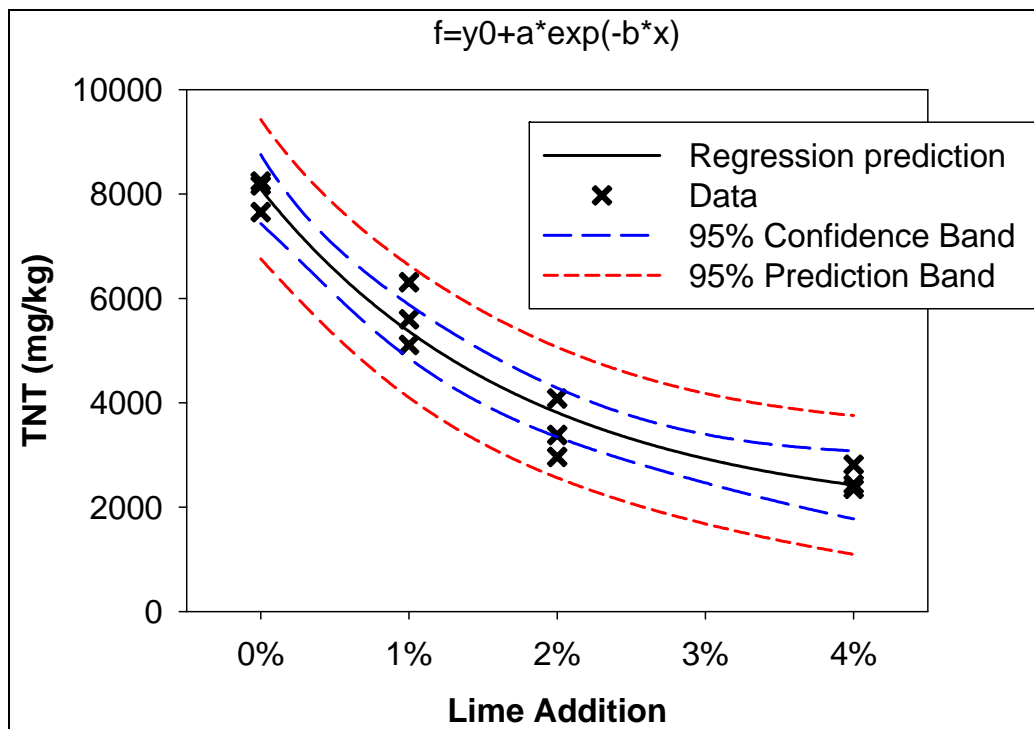


Figure 8. Non-linear regression of lime as a variable with 20% soil moisture.

with 20% moisture addition. Although the sampling/extraction process was conducted immediately after the addition of HL and water, the HL treated samples had substantially lower levels of TNT measured by the Method 8330 process. This reduction is substantially greater than predicted by the reaction rate of HL treatment.

Analysis of variance (ANOVA with Tukey test) with lime as a variable showed that all conditions were significantly different ($\alpha = 0.05$), with the exception of 2% lime addition and 4% lime addition. This is an indication that a significant relationship may exist between the amount of lime added and the results of the TNT extraction/analysis.

An exponential decay regression approaching a minimum was used to describe the data (Figure 8). This regression provided a good fit of the data with an adjusted coefficient of determination (R^2_{adj}) of 0.948. The regression indicates that a minimum concentration of approximately 1760-mg/kg of TNT is approached with increasing lime addition.

Figure 9 shows the results of a study focusing on the effect of soil moisture on the extraction and analysis of TNT (see Table 1). In this study, soil moisture was varied (0 to 20%) with constant lime addition (2%). With no moisture, the TNT concentration was close to the level found for no lime addition (see Figure 8, the 0% lime addition value). However, with just 5% moisture, the measured TNT concentration was about 50%. Higher moisture additions resulted in further, although modest, decreases. ANOVA analyses confirmed that the moisture added conditions were statistically lower than the control (no moisture added).

Figure 10 summarizes the effect of water and HL, and how acidification can improve the analytical process. Point F shows the concentration with no moisture or lime. Point A shows that with moisture alone, no effect is seen. Point D shows no effect with lime, but no moisture. However, Point B shows that with both of these parameters present, the TNT concentration is depressed. Acidification is shown in points C and I. With C, lime is present. The reported concentration was lower and the concentration between replicates is more variable. However, ANOVA analysis indicates that the concentration is not statistically significant compared to non-limed samples.

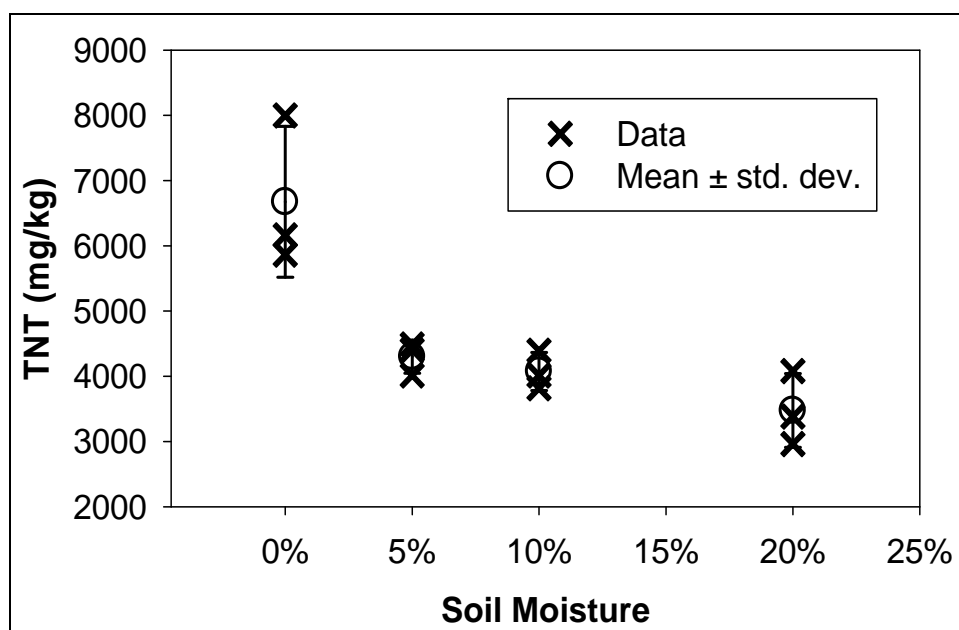


Figure 9. Variable moisture with 2% lime addition.

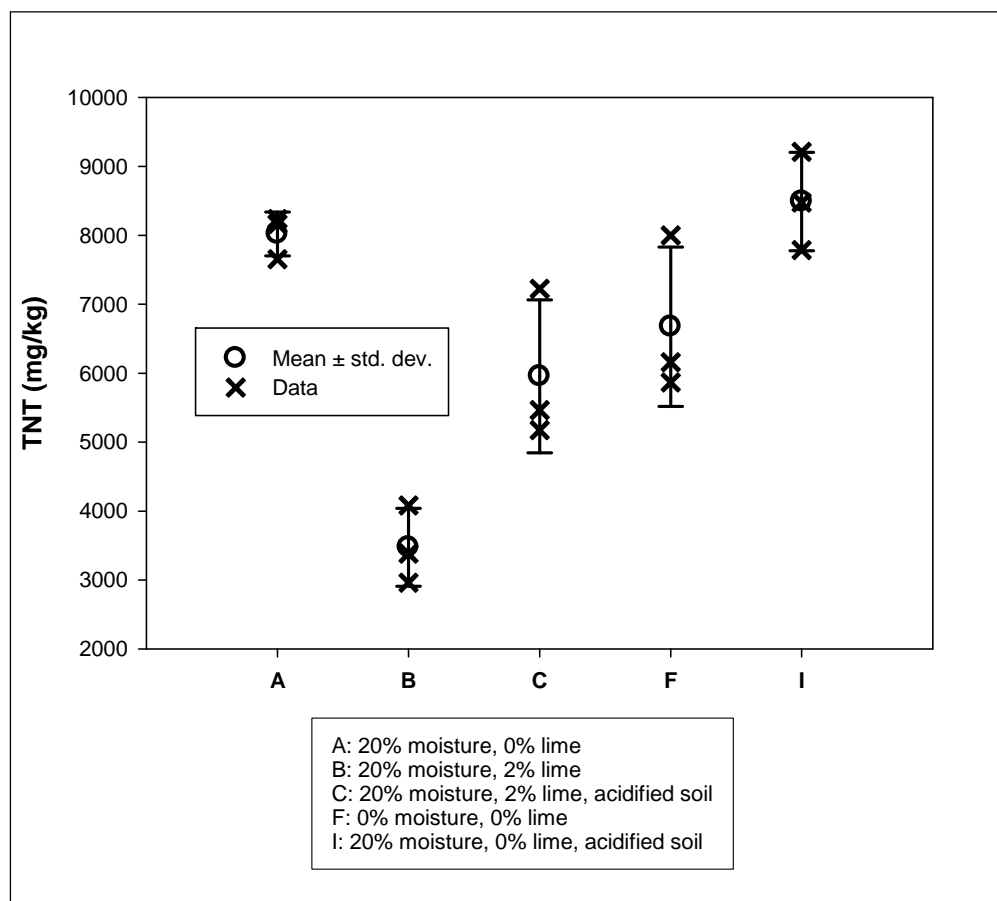


Figure 10. Effect of pre-extraction acidification of soil.

For this portion of the study, H_2SO_4 was used to affect neutralization. The reaction created substantial foaming that took up to 2 hours to dissipate. No effort was made to optimize the neutralization approach. The next portion of the study focused on developing an acidification process that can be universally used for both TNT and RDX, for a variety of possible caustic additions, and for a wide range of soil types.

Laboratory Study 2. Confirmation of False Degradation and the Acid Neutralization Effect

Sample Heterogeneity

Based on the results of the initial set of triplicate analyses (Table 2), specific soils were selected for dissolution, alkaline hydrolysis treatment, and neutralization studies. As seen in Table 3, soils with significant concentrations of explosives, either TNT, RDX or both, showed low (10% or less) standard deviations among the triplicate analyses. Soils that contained explosives at levels close to the detection limit showed higher variability within the triplicate analyses. Soils selected for further investigation of TNT transformation and neutralization techniques are: PB1, LOOW, IAAP and CE. Soils selected for further investigation of RDX transformation and neutralization techniques are: LOOW, CE, and IAAP.

Table 3. Initial concentration of TNT and RDX in sample soils as determined using SW-846 Method 8330.

Soil	TNT (mg/kg)			RDX (mg/kg)		
	AVG	STDEV	%STDEV	AVG	STDEV	%STDEV
PB1	15.97	0.39	2.45%	ND	—	—
PB2	0.85	0.04	4.39%	ND	—	—
LOOW	510.67	54.90	10.76%	314.67	4.07	1.29%
CE	2,655.08	50.55	1.90%	313.85	2.98	0.95%
IAAP	0.30	0.13	43.21%	15.97	0.39	2.45%
LSAAP	0.51	0.06	10.76%	ND	—	—

ND – non-detect, below the laboratory detection limit

Dissolution of Explosives in Water

As described in the Introduction, alkaline hydrolysis (AH) relies on the dissolution of the contaminant (in this case, an explosive) for the destructive reactions to occur. TNT and RDX are the most important explosives used by

the Army from an environmental standpoint. These compounds have some important differences in terms of solubility that may affect their reactions in an AH system. A series of selected soil extractions were performed with RO water in order to evaluate the rate at which the explosive present either as particulates or bound to the soil particles transferred into the aqueous portion of the system where base hydrolysis can occur. Four soils were analyzed for TNT and RDX (Figures 11 and 12, respectively), with results presented as the percent explosive remaining from the initial mass over time.

As can be seen in Figure 11, the four soils, IAAP, CE, LOOW and PB1 showed similar slow rates of migration of the soil-based TNT into the extraction water over time. After 20 days and four removal/replacements of one half of the extraction water volume, 80 to 90 percent of the TNT in all four soils was still associated with the solid phase. This slow rate of migration from the soil to the dissolved form is a result of the slow rate of dissolution of particulate TNT into water as well as the strong sorptive forces between soil and TNT (Larson et al. 2008a). The preparation of the soils used in the comparative studies involved grinding soils using a mortar and pestle to a point where the soils passed through a 0.075 mm sieve. Following the grinding and sieving of air-dried soils, no particulate explosive could be observed in any of the soils. From a remediation standpoint, slow dissolution is a primary reason why the pH of the pore water of a soil being treated using alkaline hydrolysis must remain elevated over an extended period of time.

Figure 12 displays results for the same water extraction experiment for RDX for the three soils IAAP, CE, and LOOW—there was no RDX in PB1. Unlike the results displayed in Figure 8 for TNT, the RDX undergoes a rapid dissolution/desorption from soil when exposed to an excess of distilled water. For all four soils, greater than 50% of the RDX present in the soil is found dissolved in the water on the first sampling (15 minutes) and at 120 hrs, after three water removal replacement cycles, all of the RDX that was initially in the soils is accounted for in the water. Poor soil sorption, as well as rapid dissolution of RDX when aqueous RDX concentrations are low, is a possible explanation for these observations.

Development of Neutralization

As indicated previously, soil pH is typically reduced over time following AH treatment. Thus, there can be cases where the neutralization step is not necessary. If, following AH treatment, the pH of the soil has fallen

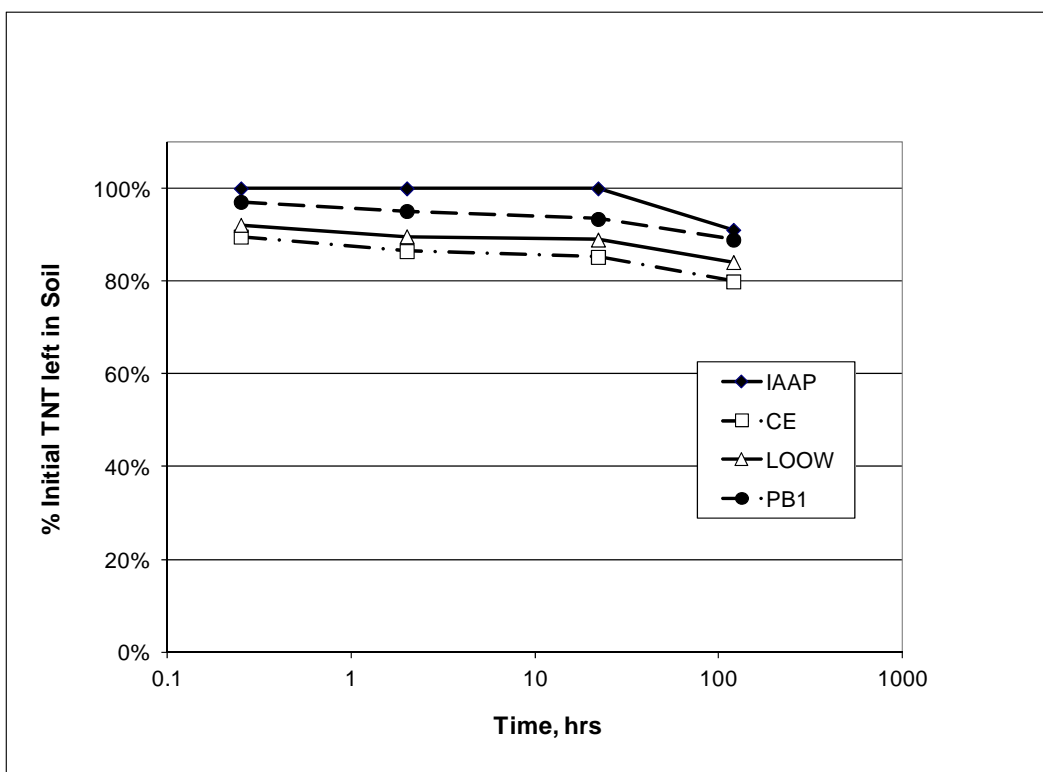


Figure 11. Percent of TNT remaining in soil compared to the initial concentration over time as determined by DDI water extraction and analysis by SW-846 Method 8330.

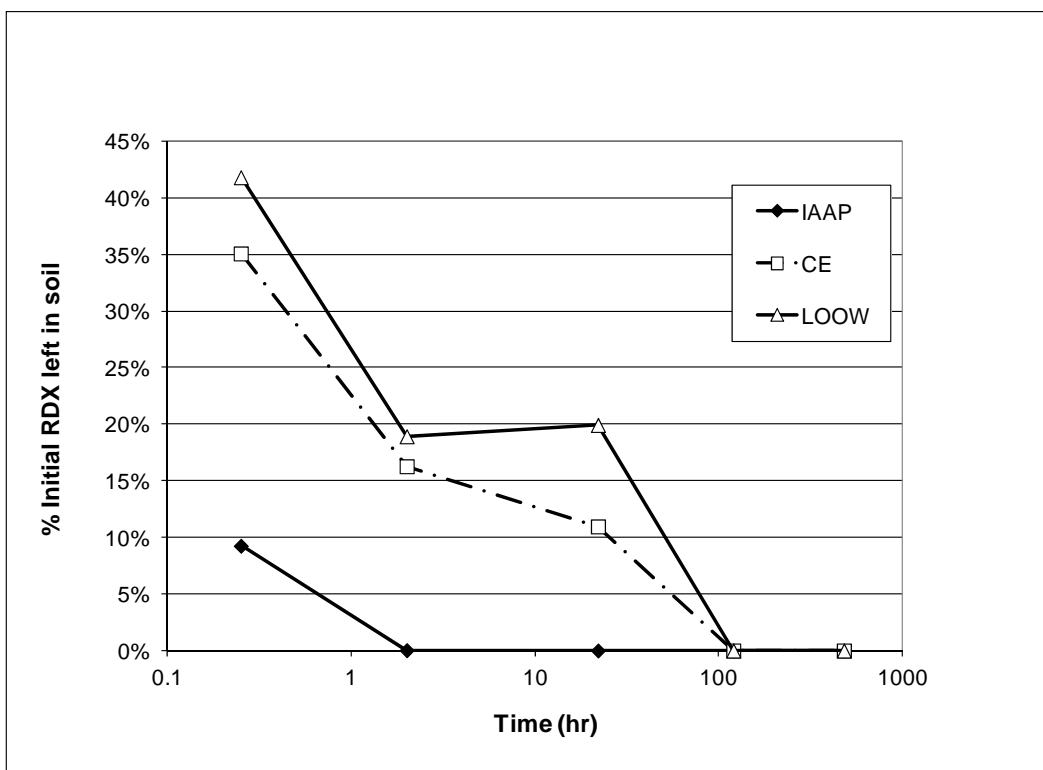


Figure 12. Percent RDX remaining in soil compared to the initial concentration over time as determined by DDI water extraction and analysis by SW-846 Method 8330.

below a pH of 10, or below the background soil pH, the neutralization step may not be necessary. However, the amount of time for the pH of the soil to fall back to a pH level that would eliminate the need to neutralize is variable, and could range from days to months, depending on site-specific factors. When implementing a soil treatment remedial action, however, there is usually an immediate need (and often contractual requirements) to determine the effectiveness of the treatment process. In addition, early determination of treatment effectiveness is strongly recommended from a quality assurance standpoint. A pro-active approach to confirmatory sampling can oftentimes be used to correct problems, to potentially modify the process to ensure that the technology is being properly implemented, prevent the need to retreat soil, and reduce the potential for costly contract modifications. If lime is being used, it is generally advisable to allow more time for the AH reaction to occur before collecting confirmatory samples, than if NaOH is being used.

Remediation projects conducted with high water contents, such as slurry-based treatments, would likely have fewer issues with residual pH, as the high water content would promote mass transfer out of the solid phase. However, due to the fact that the pH of the entire system must be maintained above 10 to promote the hydrolysis reactions, there would still be potential for false positive degradation results. The acid neutralization approach developed in this study would be appropriate for slurry applications.

Buffer-only Neutralization

The first neutralization study compared explosives concentrations from LOOW and CE soil. Near immediate (15 min) neutralization of a NaOH treated sample using one equivalent of NaH_2PO_4 returned a result from EPA Method 8330 analysis for RDX that was, within one standard deviation, identical to the analysis of a sample that was not treated with NaOH (Figure 13). When HL was used as the AH agent, however, neutralization was not effective at returning an RDX concentration that reflected the true concentration of RDX at the time of neutralization. For both LOOW and CE, less than 50% recovery was observed following neutralization (Figure 10).

Because NaOH is a strong base that is highly soluble in water, there appears to be a rapid reaction between the NaH_2PO_4 and the dissolved NaOH, reducing the system pH to below the pH at which AH of RDX occurs. HL,

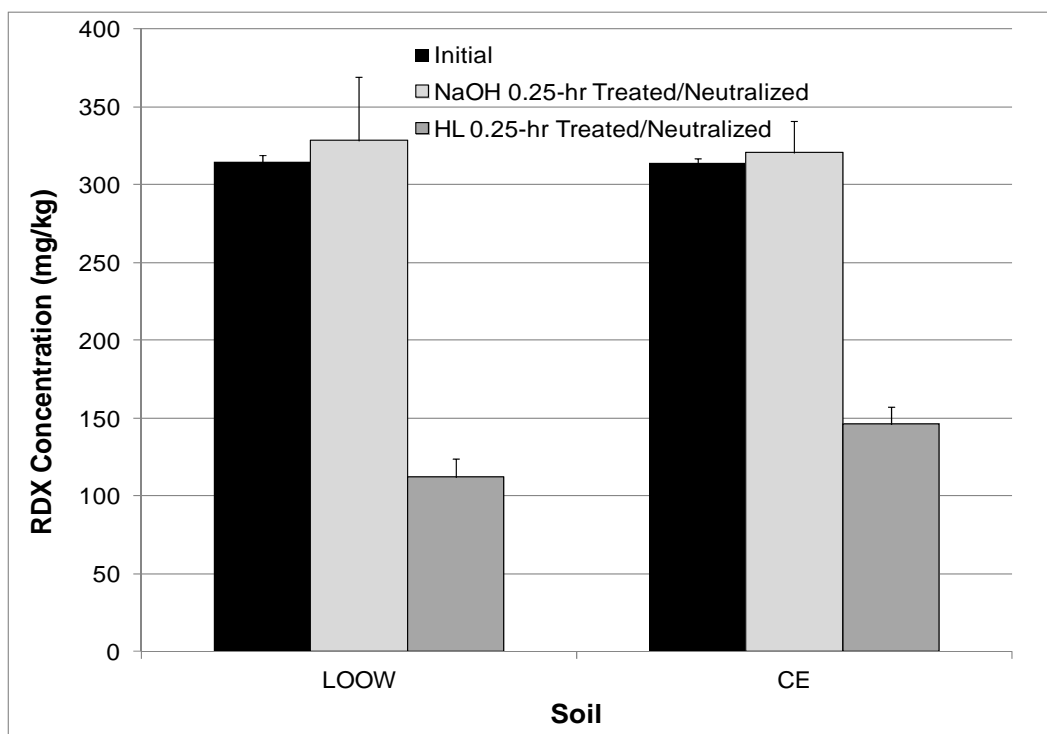


Figure 13. Initial average RDX concentration (mg/kg) compared to concentration immediately following (0.25-hr) alkaline hydrolysis with sample neutralization for soils from LOOW and CE (n=3). Error bars are one standard deviation.

on the other hand, dissolves more slowly, releasing hydroxide ions over a greater span of time. Even though there was sufficient NaH_2PO_4 in the system to neutralize the excess hydroxide ion, the hydroxide ions slowly and continuously enter the aqueous portion of the system. Localized areas of high pH pore water occur throughout the soil surrounding the lime particles. These areas are long-lived enough, due to the low solubility of HL, to continue degrading RDX. In summary, the slow reaction rate between HL and the buffer-only system does not prevent the AH reaction from occurring during the analytical procedure.

Buffer-Acid Neutralization

In order to provide a more universal neutralization procedure for soils that have been amended with either NaOH or HL, a strong acid (in the present studies, that was phosphoric acid (H_3PO_4)) must be incorporated into the neutralization system. The acid can rapidly dissolve the HL along with the NaH_2PO_4 buffer that is required in order to keep the sample from becoming too acidic for analysis. Figure 14 shows the results of initial RDX concentrations, and RDX concentrations obtained using buffer only (Limed and Neutralized -1) or using using buffer and strong acid (Limed and Neutralized -2).

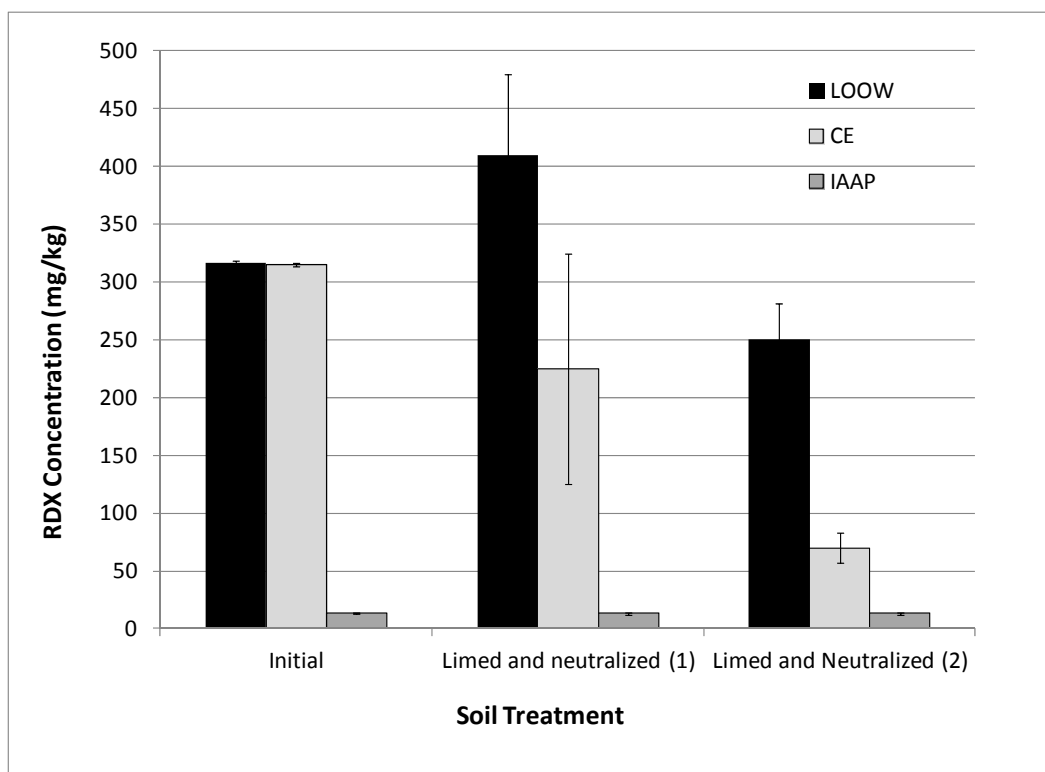


Figure 14. Average concentration of RDX in soil initially and after treatment with NaOH and neutralization (mg/kg, n=3)

Comfort et al. (2003) examined the loss of RDX at low pH and reported no appreciable loss even at pH as low as 2.02. For soils containing RDX, sufficient strong acid should be used in order to facilitate the dissolution and neutralization of the caustic material. Acids used in this study do not pose a hazard of lowering the pH to the point where RDX degradation may occur.

TNT is much more tolerant of reduced pH solutions than RDX. This simplifies the neutralization of soils where TNT is the predominant contaminant of concern. As shown in Figure 15, the TNT levels for Limed and Neutralized (1) samples and for for Limed and Neutralized (2) are similar to the TNT concentrations obtained from the analysis of soil samples that have not been treated with an alkaline hydrolysis material. This study did not analyze the treated soils for the DNTs, amino-DNTs or the diamino-DNTs. Bhadra et al. (1999) reported that acid hydrolysis successfully degraded the amino-DNT degradation products of TNT.

The ability to double the dose of the strong acid in these soils provides a means to standardize the neutralization step throughout a treatment. The actual number of equivalents of hydroxide present after NaOH and HL soil treatment will decrease with time via several mechanisms, including

reactions with carbonic acid (from the dissolution of carbon dioxide in the atmosphere), buffering by soil minerals, reactions with humic or organic acids, and gradual leaching of the caustic material.

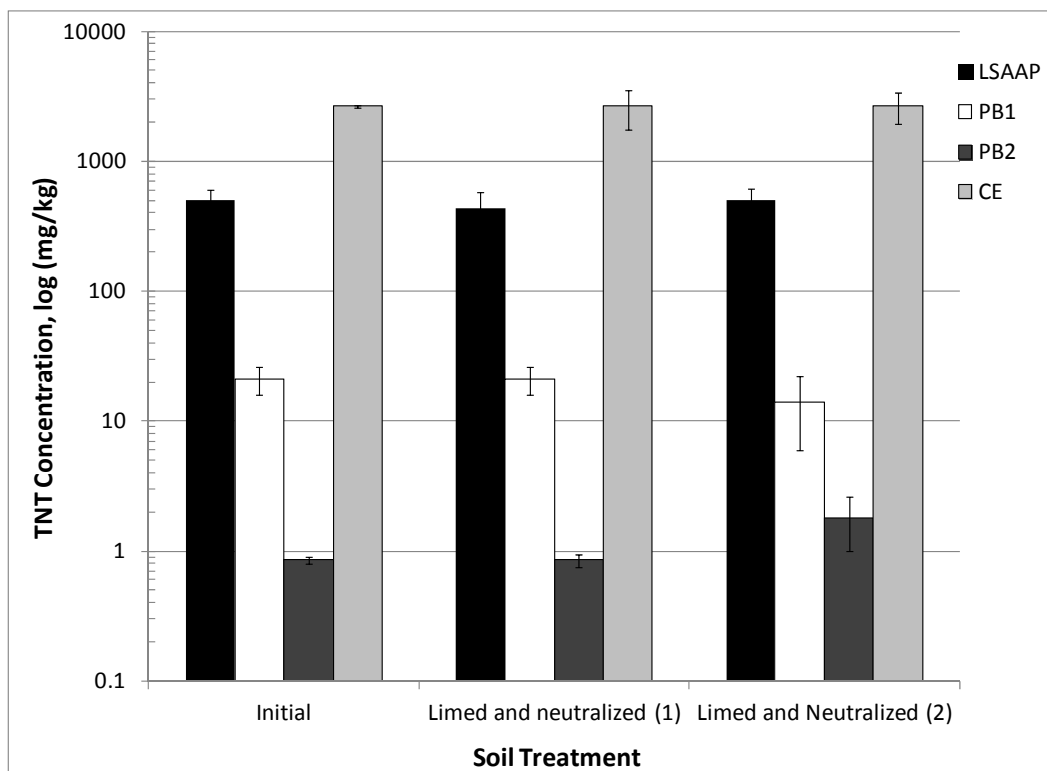


Figure 15. Average concentration of TNT in soils initially and after treatment with NaOH and neutralization, where Limed and Neutralized (1) entails neutralization using buffer only and Limed and Neutralized (2) entails neutralization using buffer and strong acid. (mg/kg, n=3)

4 Conclusions/Discussion

- The combination of residual caustic material and moisture in soils treated with AH can lead to lower analytical results for explosives; this may lead to the mistaken conclusion that more degradation has occurred than what has actually happened. It can also lead researchers to report false degradation as legitimate results.
- It is possible to neutralize the caustic hydrolysis materials after they are placed in soils to get a more accurate concentration when performing the traditional USEPA Method 8330 analytical procedures.
- Treatment systems using HL are more prone to extraction errors than systems using NaOH, although neutralization improves the accuracy of both treatment approaches.
- The specific mass of the neutralization materials is dependent on the amount of hydroxide source introduced, the type of hydroxide source used, the specific contaminants of concern, and the extent of degradation of the hydroxide source over the course of the remedial action.
- If base hydrolysis is going to be monitored over time and/or for completeness of degradation, then neutralization prior to sonication is the best means to collect quality data. For a given system, a generic neutralization mixture can be prepared for on-site addition of soil or used immediately upon arriving at the laboratory. The neutralized samples can then be air dried, sonicated, and analyzed.
- Care must be taken to ensure that acid neutralization does not result in acid reactions that degrade RDX. The process developed for this study does not reach pHs low enough to result in RDX removal.
- ERDC has developed a neutralization procedure that can be used for alkaline hydrolysis approaches using up to 10% caustic addition (most systems are less than 5%). A combination of H_3PO_4 and NaH_2PO_4 are utilized in the procedure.
- For remedial actions using alkaline hydrolysis, the scope of work for the action should include neutralization of all post-treatment samples with appropriate control samples prepared in order to ensure that neutralization is achieved and that the pH of the neutralized system is not highly acidic, especially for RDX quantization.
- If lime is being used instead of NaOH, it is generally advisable to allow more time for the AH reaction to occur before collecting confirmatory

samples. Waiting seventy-two (72) hours may be a good guideline to follow, although kinetic studies may be useful to consider.

- Due to the shorter activation time of NaOH, respiking might be necessary in AH projects that utilize this caustic source..
- Table 4 summarizes recommended acids for neutralization depending on the explosives constituents and the caustic used in an AH treatment scenario.

Table 4. Recommended pH adjustment protocol for various contaminant mixtures and AH reagents.

Alkaline Hydrolysis Reagent	Contaminants present in soil	
	TNT, DNT only	TNT, DNT and RDX
Hydrated lime	buffer + SA, or SA	buffer + SA
NaOH	buffer + SA, SA, or buffer	buffer + SA, or buffer

Buffer = buffered acid (NaH_2PO_4),

SA = strong acid (i.e. H_3PO_4)

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14. ABSTRACT: Alkaline hydrolysis has been used in several laboratory studies and field demonstrations for the treatment of energetic compounds (particularly, 2,4,6-trinitrotoluene (TNT), dinitrotoluene (DNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)) in soil. The application of alkaline hydrolysis for treatment of soil involves mixing a caustic source material with soil. Two caustic materials have been explored, calcitic hydrated lime [Ca(OH) ₂ , HL] and sodium hydroxide (NaOH). Evaluation of explosives removal is routinely performed using SW-846 Method 8330. This method was developed before the advent of alkaline hydrolysis treatment, and recent studies have indicated that some errors can occur when this method is applied to alkaline hydrolysis samples. This report documents the results of a field study, conducted to demonstrate the issue of false degradation in field-collected samples. The field study was followed by two laboratory studies: the first to confirm false degradation as a phenomenon and the second to develop an appropriate acid neutralization method. Results proved that false degradation can occur with alkaline hydrolysis (AH) samples, particularly if residual caustic material and moisture are present in the sample. Treatment systems using HL are more prone to extraction errors than systems using NaOH, although neutralization improves the accuracy of both treatment approaches. ERDC-EL has developed a neutralization method that can be used for alkaline hydrolysis approaches using up to 10% caustic addition (most systems are less than 5%) and a combination of H ₃ PO ₄ and NaH ₂ PO ₄ . For remedial actions using alkaline hydrolysis, the scope of work for the action should include neutralization of all post- treatment samples, with appropriate control samples prepared in order to ensure that neutralization is achieved.					
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